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Distribution of Arsenic in Three Geochemical Fractions of Surface Sediments from Coastal Sites of Sonora, Gulf of California, Mexico

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Arsenic is widely distributed in marine environments (Langdon et al. 2003). Arsenic interaction with sediments is determined by chemical and physiochemical properties. Toxic of arsenic to organisms depends on the speciation and biological factors. The principal species of arsenic are arsenate, arsenite and a large number of organic species. Since sediments are a sink of arsenic in aquatic environments, the study of this element in those reservoirs may indicate the pollution degree of the system. In addition, some environmental changes produce transformation and mobilization of arsenic from sediment to biota (Langdon et al. 2003). Bioavailable arsenic estimation based in extraction schemes for chemical speciation analysis is required for a toxicity evaluation (Prego and Cobelo-García 2003). An operational fractionation using selective chemical extraction solutions (Tessier et al. 1979; Mahan et al. 1987), performed in a three steps method is easy and suitable to determine the toxic potential of sediments (Carapeto and Purchase, 2000).

Sonora state is located in Northwest Mexico (Figure 1). Previous work by Wyatt et al. (1998) reported incidence of arsenic in water supplies of some cities, 8.92% of samples exceeded the allowed limit (0.05 μg/mL) established by World Health Organization (WHO, 1993). Arsenic mobilization from ground to water was associated with fluoride levels, indicating a common pathway of toxicity and a wide distribution of arsenic in the studied sites (Wyatt et al. 1998). Exposure to species of arsenic like arsenite (the more toxic inorganic form) has been related to neurotoxicity and low growth rates in aquatic organisms (Bellucci et al. 2002).

Sonora is one of the principal fishery producers in Mexico (CONAPESCA, 2002). In a previous study, García-Rico et al. (2003) detected a range of 0.09-7.71 μg/g of total arsenic in surface sediments of oyster farms of the state. Because some concentrations were near the minimal toxic effect level (7 μg/g) in sediments (Bellucci et al. 2002), it is necessary to evaluate the potential risk of arsenic in organisms, determining its relative bioavailability in the sediment. For this reason, the aim of this study was to evaluate arsenic distribution in geochemical fractions of surface sediment of four oyster culture sites in the Sonora coast.

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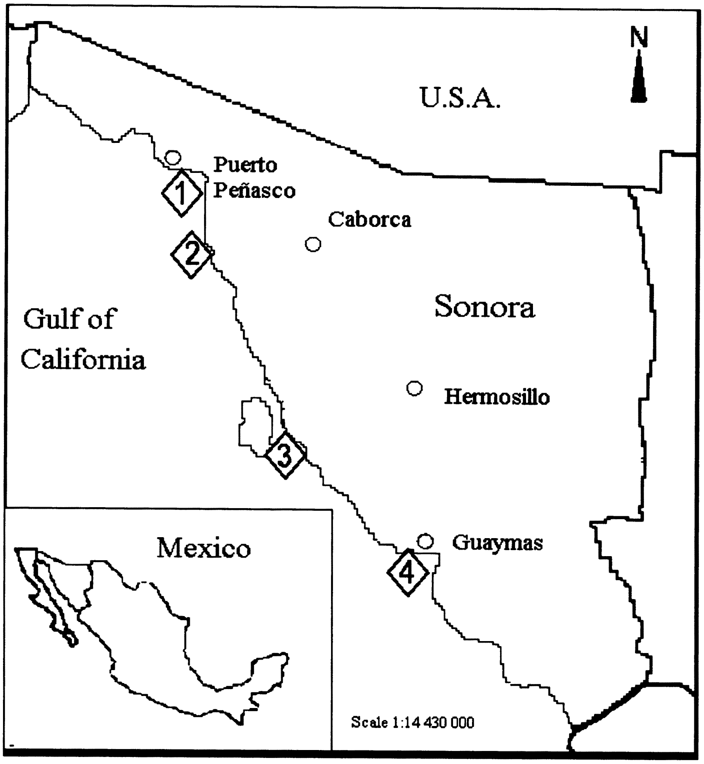

Figure 1. Localization of four coastal sites in Sonora State (site 1=Puerto Peñasco, site 2=Caborca, site 3= Hermosillo, site 4= Guaymas)

MATERIALS AND METHODS

Fifty-four surface sediment samples were collected in four study sites of the Sonora state (Figure 1) from February to August 1999. The sample sites were selected according to their proximity to potential pollution sources and to oyster culture areas. Each sediment sample was composed of three sub-samples each one taken in a 1 m radiu and at low tide. Plastic spoons and polyethylene containers previously washed with 20% v/v nitric acid were used. Coarse materials (> 5 mm) were removed, then sediment was homogenized using a plastic spoon. Samples were dried at 55°C for 24 h and stored in hermetic polyethylene bags until analysis.

A microwave selective extraction scheme with a MARSX system (CEM Co), adapted from Mahan et al. (1987), was used (Table 1). Considering the toxic potential fractions reported by Carapeto and Purchase (2000), arsenic concentration was determined in 3 fractions: exchangeable (EF), bound to organic matter (OMF) and residual (RF); by hydride vapour generation (VARIAN VGA-76) coupled to an atomic absorption spectrophotometer (VARIAN SpectrAA-20). Organic matter was determined by the Gaudette et al. (1974) method and

Table 1. Microwave assisted extraction scheme. Adapted from Mahan et al. (1987) and Carapeto and Purchase (2000).

Fraction	Reagent	Extractat volume (mL)	Experimental conditions
Exchangeable (EF)	1 M $MgCl_2$, pH 7	10	4 min at 100°C, 100 psi
Organic matter (OMF) step 1:	1 M CH_3COONa, pH 5 adjusted with CH_3COOH	10	4 min at 100°C,100 psi
step 2:	0.04 M NH_2OH-HCl, in 25 % v/v CH_3COOH	10	4 min at 100°C, 100 psi
	As step 2	5	
	As step 2	5	
	As step 2	5	
step 3:	30 % H_2O_2 pH 2 adjusted with HNO_3	10	4 min at 75°C, 100 psi
step 4:	3.2 M $CH_3COOHNH_4$ in 20 % v/v HNO_3	10	Manual shaking (1 min)
Residual (RF)			
step 1:	HNO_3	4	15 min at 175°C, 200 psi
	HF	4	
	HCl	1	1 min at 200°C, 200 psi
step 2:	4 % v/v H_3BO_3	25	15 min at 165°C, 60 psi

carbonate content was analyzed according to Rauret et al. (1988). For quality control purposes, duplicates and blanks were analyzed during the procedure. Accuracy of analysis was evaluated by sequential extraction of arsenic in the Certified Reference Material PACS-2 (National Research Council of Canada). Percent recovery mean (n=6) was 98.74% and the variation coefficient was <8 %. Detection limits (ng/g dry wt) in the fractions were: EF= 2.21, OMF= 3.51 and RF= 4.80. Statistical analysis were performed using ANOVA-General Linear Model, Fisher's LDS mean comparison and Pearson correlations (NCSS, 1996). For the statistical purpose analysis, detection limits were used in cases where arsenic was not detected.

RESULTS AND DISCUSSION

Surface sediments were characterized by low organic carbon, with a range of 0.35-2.19% (mean=1.28%), in agreement with other reported values in coastal sediments (Méndez et al. 1998; Shumilin et al. 2001). This reflects a low anthropogenic impact by local discharges in studied sites and it may limit the methylation of arsenic by microbial activity (Villa-Lojo et al. 1997). In contrast, a wide range of carbonate content was observed (0.57-71.6%, mean=17.58%), with the highest mean in Guaymas sediments (60.75%). In this site, abundant shell fragments of calcareous organisms were observed, carbonates are incorporated to sediments by degradation process. Carbonate compounds may reduce arsenic mobility and toxicity, by linking them to cationic species (Davis 2000).

Distribution of arsenic in the fractions of surface sediments is presented in Table 2. No significant differences ($p>0.05$) in mean of arsenic concentration among fractions EF and OMF were detected. In addition, the residual fraction (RF) showed the highest ($p<0.05$) mean concentration of arsenic, linking most of the semi-metal (>95%). RF is characterized by quartz net that immobilizes the element (Tessier et al. 1979). Because it is weakly linked and may be mobilized to biota under specific environmental conditions, arsenic concentration in EF and OMF fractions are recognized as the principal reservoirs of biologically available element (Tessier et al. 1979; Carapeto and Purchase 2000). Consequently, potentially bioavailable arsenic in surface sediment was low (0.33 μg/g), representing <5% of the total arsenic concentration, which is considered as minimal toxic risk (Bellucci et al. 2002).

Arsenic concentrations found in surface sediments of the study areas are shown in Table 2. Each site show a similar concentration of arsenic in the EF and OMF fractions, but slightly higher in Caborca and Hermosillo sites. Previously, Wyatt et al. (1998) reported high arsenic levels in well water in these study sites. Both sites are associated to agricultural districts that use ground water for irrigation, it is possible that arsenic has been mobilized from deep volcanic deposits into the watertable that is used for agriculture and drinking needs in these cities. Arsenic concentrations may be also related to fertilizers that could be used in intensive agriculture (Davis 2000; Langdon et al. 2003).

The total range of concentration of arsenic found was 0.05-13.54 μg/g (Table 2), which is notably lower than those reported by Bellucci et al. (2002) (5-132 μg/g) and Jung et al (2002) (119-2400 μg/g) in surface sediments of industrial areas, indicating a low anthropogenic impact in the study sites. The range of total arsenic concentration in the three fractions (EF+OMF+RF) from the four sites was 5.67-8.97 μg/g, slightly greater than previously reported in the same studied sites (García-Rico et al. 2003), possibly as a result of the microwave selective extraction scheme used. Shumilin et al. (2001) reported an arsenic range of 0.83-44.4 μg/g in surface sediments of La Paz Lagoon (Mexico). These authors suggest an arsenic association to volcanic minerals carried by streams to lagoon. This difference could imply a low volcanic mineral content in the surface sediments of the four sites studied and support the idea that arsenic concentrations in Hermosillo and Caborca sites are related to minerals transported by groundwater.

Total arsenic concentrations found in this study were similar to those reported in non-polluted sediments (Bellucci et al. 2002; Prego and Cobelo-García 2003) and the majority of arsenic was linked to the residual fraction (Table 2). However, arsenic may mobilize to bioavailable fractions by changes in environmental factors (e.g. pH, salinity and redox potential), increasing its toxic potential to

Table 2. Arsenic concentrations (µg/g dry wt), total and by sites of study, in geochemical fractions of surface sediments[1].

Site	Fraction	Mean (± SD)	Minimum	Maximum
Total	Exchangeable (EF)	0.10^{a} (0.04)	0.05	0.18
	Bound to organic matter (OMF)	0.23^{a} (0.04)	0.05	0.24
	Residual (RF)	6.59^{b} (3.47)	1.59	13.54
	EF+OMF+RF	6.92	0.05	13.54
P. Peñasco	Exchangeable (EF)	0.08^{a} (0.02)	0.05	0.13
	Bound to organic matter (OMF)	0.23^{a} (0.05)	0.05	0.24
	Residual (RF)	6.20^{b} (2.39)	1.59	8.64
	EF+OMF+RF	6.51	0.05	8.64
Caborca	Exchangeable (EF)	0.11^{a} (0.03)	0.08	0.15
	Bound to organic matter (OMF)	0.21^{a} (0.02)	0.06	0.23
	Residual (RF)	5.35^{b} (3.38)	1.81	11.00
	EF+OMF+RF	5.67	0.06	11.00
Hermosillo	Exchangeable (EF)	0.14^{a} (0.04)	0.09	0.18
	Bound to organic matter (OMF)	0.21^{a} (0.02)	0.08	0.22
	Residual (RF)	7.30^{b} (4.47)	2.11	13.54
	EF+OMF+RF	7.65	0.06	13.54
Guaymas	Exchangeable (EF)	0.07^{a} (--)	0.07	0.07
	Bound to organic matter (OMF)	0.22^{a} (0.02)	0.05	0.09
	Residual (RF)	8.68^{b} (4.42)	3.00	12.00
	EF+OMF+RF	8.97	0.05	12.00

[1] Different letter by column means significant difference at α=0.05.

biota and producing bioaccumulation. In conclusion, the studied sites are pristine in arsenic levels but is important to obtain more information about changes in arsenic concentration in sediment, water, and biomonitor organisms to detect alterations of arsenic bioavailability.

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